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(54) Title of invention: Impermeable swollen graphite molded body

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Specification

1. Title of Invention

Impermeable swollen graphite molded body

2. Scope of Patent Claims

1) An impermeable swollen graphite molded body formed by impregnating with resin a molded body of swollen graphite powder or a molded body that was molded by layering said molded bodies, and rinsing away the resin on the surface of the molded body, then heat-curing it.

3. Detailed Explanation of the Invention

This invention pertains to an impermeable swollen graphite molded body. It is applied to fuel cell partition plates and so forth.

The characteristics required of fuel cell partition plates are corrosion resistance against electrolytes, electrical conductivity, and impermeability to air. Corrosion-resistant alloys and carbon materials have been offered as materials that satisfy these requirements. However, all of these have the drawback that materials costs and processing costs are high. For the sake of cost reduction, swollen graphite sheet has been offered as a material that aligns with these goals, but this sheet is corrosive in electrolytes in its direction of thickness, and it has a small volume through which fuel and air pass so that its resistance to passage is large. As a result, there are the problems that supplying fuel is not inexpensive, and constant power is not obtained Thus, improvements are required.

The purpose of this invention is to provide an impermeable swollen graphite molded body that resolves the aforementioned problems.

This invention pertains to an impermeable swollen graphite molded body formed by impregnating with resin a molded body of swollen graphite powder or a molded body that was molded by layering said molded bodies, and rinsing away the resin on the surface of the molded body, then heat-curing it.

The swollen graphite powder used in this invention is that which has bulk density of about 0.001–0.02 g/cm^3. This swollen graphite powder alone is made into a plate-shape molded body or a bipolar-type grooved molded body of bulk density 0.1–2.0 g/cm^3, preferably 0.5–1.8 g/cm^3, formed by compression-molding by passing it through a press or between rollers, or a plate-shaped molded body or bipolar-type grooved molded body of bulk density 1.5–2.0 g/cm^3, preferably 1.6–1.8 g/cm^3, formed by layering plate-shaped pre-molded bodies molded to bulk density of 0.1–1.4 g/cm^3, and then compression-molding them in a press or between rollers. The plate thickness of the molded body can be suitably selected in the range from about 0.2 cm to several cm.

This molded body is immersed for a time from several minutes to 20 hours in a liquid resin bath whose solid content is at least 10 weight %, and after the molded body surface is rinsed with a solvent, it is heat-cured at 50–200°C. To correct for warping of the molded body during heat-curing, it is preferably cured sandwiched between [illegible] plates.

The amount of resin impregnated in the molded body is adjusted so as to be 0.5–10 weight %, preferably 2–7 weight %. As the resin that is used, a heat-curable resin such as phenol resin, melamine resin, melamine-modified phenol resin, epoxy resin, furan resin and so forth is selected.

Implementation examples are explained below.

Implementation example 1

100 g of Madagascar [illegible] graphite (average 50 mesh) was immersed for 1 hour in a mixed liquid of 300 g of concentrated sulfuric acid and 100 g of concentrated nitric acid, then it was rinsed with water and dehydrated, then it was rapidly heated to 1000°C, and the obtained swollen graphite powder of bulk density 0.005 g/cm^3 was compression-molded by being passed between rollers, and a molded body of sheet thickness 0.5 mm and bulk density 1.4 g/cm^3 was obtained. Then, this molded body was immersed for 12 hours in melamine-modified phenol resin PR-4060 (trade name, made by Hitachi Kasei Kogyo), and the attached resin on the surface of the molded body was rinsed away with toluene. After that, heat-curing was performed by heating to 160°C at a heating rate of 25°C/hour, and a molded body that was impregnated with 2.5% resin by weight was obtained.

Implementation example 2

Swollen graphite powder of bulk density approximately 0.005 g/cm^3 was compression-molded by being passed through rollers, and a molded body of sheet thickness 1.0 cm and bulk density 0.5 g/cm^3 was obtained. Several 14 cm × 14 cm tablets were cut from this molded body and layered on top of each other, then molded at a pressure of 800 kg/cm^2 with a mold that was 14 cm × 14 cm in area, that had protrusions 1 mm high and 1.5 mm wide with a spacing of 3 mm on both surfaces, such that their grids were perpendicular to each other. This grooved molded body was immersed in furan resin VF-303 (trade name, made by Hitachi Kasei Kogyo) for 12 hours, then its surface was rinsed with toluene. Heat-curing was performed in the same way as in implementation example 1. The resin content of this product was 3.2 weight %.

Table 1 shows corrosion resistance in the electrolyte (3 Mol solution of H_2SO_4) and characteristics after resin impregnation for the swollen graphite molded bodies obtained in the implementation examples.

Table 1 Effect of resin impregnation

	Impregnated	Bending strength (kg/cm^2)	Resistivity in direction of thickness (mΩ-cm)	Air permeability (cm^2/s)	Swelling ratio in direction of thickness (%)
Implementation example 1	No	1.2	90	$2 \times 10^{-?}$	1.3
	Yes	1.8	90	0	0.5
Implementation example 2	No	1.5	75	$3 \times 10^{-?}$	1.2
	Yes	2.4	75	0	0

As is clear from Table 1, by impregnating with heat-cured resin, the swelling ratio is greatly reduced, air permeability is reduced to zero, and bending strength is increased.

By this invention, by impregnating a swollen graphite molded body with resin, air permeability is greatly improved without losing the electrical characteristics of the swollen graphite molded body, and it becomes impermeable, and mechanical strength is increased, and corrosion in the electrolyte is nearly eliminated.

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⑤発明の名称　不浸透性膨張黒鉛成形体

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明　細　書

1. 発明の名称

不浸透性膨張黒鉛成形体

2. 特許請求の範囲

1. 膨張黒鉛粉末の成形体または粗成形体を積層して成形した成形体に樹脂を含浸し、成形体の表面の樹脂を洗浄除去した後、加熱硬化させてなる不浸透性膨張黒鉛成形体。

3. 発明の詳細な説明

本発明は、不浸透性膨張黒鉛成形体に関するものであり、その用途は燃料電池用隔壁板などに供されるものである。

燃料電池用隔壁板は、その特性として電解液に対する耐食性、電気伝導性、気体の不透過性が必要とされる。これらの特性を満たす材料として耐食性合金と炭素材料が提供されている。しかし、いずれも材料費、加工費が高いことが欠点とされている。価格低減のために膨張黒鉛シートがこの目的に合う材料として提供されたが、このシートは電解液中で厚さ方向に膨潤し、燃料、空気の通路部体積が小さくなり、通過抵抗が大きくなるため燃料の供給が不安定になり、一定出力の電力を得られなくなる問題を生じ、この改善が必要とされていた。

本発明は上記した問題を解消する不浸透性膨張黒鉛成形体を提供することを目的とする。

本発明は、膨張黒鉛粉末の成形体または粗成形体を積層して成形した成形体に、樹脂を含浸し、成形体の表面の樹脂を洗浄除去した後、加熱硬化させてなる不浸透性膨張黒鉛成形体に関する。

本発明で用いる膨張黒鉛粉末は嵩密度0.001～0.02g/cm³程度のものが用いられる。この膨張黒鉛粉末を単独で、プレスまたはロール間を通して圧縮成形し、嵩密度が0.1～2.0g/cm³好ましくは0.5～1.8g/cm³の板状成形体か、パイポーラタイプの枠付成形体とするか、または嵩密度が0.1～1.4g/cm³に成形された板状予備成形体を積層し、プレスまたはロール間で圧縮成形し嵩密度1.5～2.0g/cm³好ましくは1.6～1.8g/cm³の板状成形体か、パイポーラタイプ枠付成形体と

する。成形体の板厚は0.2mm程度から数mmまで通常選定することができる。

この成形体に固形分濃10重量%以上に調製された液状樹脂バスに数分から20時間程度浸漬され、取出して成形体表面を洗浄された後、50～200℃で加熱硬化される。加熱硬化の際、成形体の反りを矯正するため、鏡板に挟んで硬化させることが好ましい。

成形体に含浸される樹脂量は0.5～10重量%、好ましくは2～7重量%になるよう調整される。使用される樹脂としては、フェノール樹脂、メラミン樹脂、メラミン変性フェノール樹脂、エポキシ樹脂、フラン樹脂などの熱硬化性樹脂が適宜される。

次に実施例を説明する。

実施例1

マダガスカル産鱗状黒鉛（平均50メッシュ）100gを濃硫酸300gと濃硝酸100gの混液に1時間浸漬後、水洗、脱水し次いで1000℃に急速加熱して得られる高密度0.005g/cm³の膨張黒鉛粉末をロール間を通して圧縮成形し厚0.5mm、高密度1.4g/cm³の成形体を得た。次いでこの成形体をメラミン変性フェノール樹脂PR-4060（日立化成工業製、商品名）中に12時間浸漬し、成形体の表面の付着樹脂をトルエンで洗浄除去した。その後室温から25℃/hで160℃まで昇温して、加熱硬化を行ない厚さ25%の樹脂が含浸された成形体を得た。

実施例2

高圧成形0.005g/cm³の膨張黒鉛粉末をロール間を通して圧縮成形し、厚1.0mm、高密度0.5g/cm³の成形体を得た。その成形体から14cm×14cmの面積に切断したタブレットを数枚積層し、14cm×14cmの面積で両面に幅1.5cm、高さ1mmの凸状突起を有し、突起間の間隔3mmで片面の縦と直交するような成形金型で、面圧300kg/cm²で成形した。その得た成形体をフラン樹脂VP-303（日立化成工業製、商品名）中に12時間浸漬した後、その表面をトルエンで洗浄した。加熱硬化は、実施例1と同条件で行なつた。

本品の樹脂含有量は3.2重量%であつた。

実施例で得られた膨張黒鉛成形体について、樹脂含浸前後の物性および電解液（H_2SO_4の3Mol溶液）中での膨潤率を第1表に示す。

第1表　樹脂含浸の効果

	含浸有無	曲げ強度 (kg/cm²)	比抵抗 厚み方向 (mΩ-cm)	通気率 (cm²/s)	膨潤率 厚み方向 (%)
実施例1	無	1.2	90	2×10^{-6}	13
	有	1.8	90	0	0.5
実施例2	無	1.5	75	3×10^{-5}	12
	有	2.4	75	0	0

第1表から明らかなように、熱硬化性樹脂を含浸することにより、膨潤率が著しく低下し、通気率が零となり、曲げ強さも増大することがつかる。

本発明によれば膨張黒鉛成形体に樹脂を含浸することにより、膨張黒鉛成形体のもつ電気特性を損うことなく、通気率が大幅に改善され、不浸透になるとともに、機械的強度が増大し、電解液中での膨潤をほとんどなくすることができる。